

Introduction: Evaluating the Benefits and Potential Risks of Disinfectants in Drinking Water Treatment

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Probably the most significant public health measure introduced within the last 100 years has been the introduction of chlorine widely as a disinfectant for drinking water. Of course, not only chlorine but other oxidants also have been used, like ozone and chlorine dioxide in other parts of the world to a much greater extent than in the United States. The benefits are great and obvious. The issue for this conference is the possibility that there may be some subtle disbenefits that relate to the widespread use of these oxidants. We must consider that these oxidant chemicals and their by-products and their degradation products are the most ubiquitous organic chemical contaminants in drinking water and the most significant in terms of quantity and population exposure.

In the United States more than 150 million people consume disinfected water. Milligram amounts of chlorine and milligram amounts of by-products are being added to the water in the course of water treatment. Because of our familiarity with chlorine and chloroform, there is a great tendency to not take it very seriously if there are some risks associated. I think we would be extremely upset if various organic chemicals were being detected in drinking water coming from industrial discharges at the concentration levels that we find trihalomethanes (THMs) and other organic chemicals which are derived from the disinfection process. There is no particular reason why one should treat them differently toxicologically, but there are reasons why one should treat them differently in the sense of ultimate benefit of the process that produced them relative to potential risks.

The benefits of oxidation and disinfection of drinking water are many and we do not have to defend that. But, what is the issue in our regulatory

context is the possibility that there may be some disbenefits, and it is essential to quantify those disbenefits and to minimize them while maximizing the benefit side of the equation. The amazing thing is that in the approximately 100 years since disinfectants were introduced into water treatment, there is still so little understanding of the toxicology of these chemicals and their by-products. Remember, these are the most widely used chemicals in water treatment, and there is such a small amount of information available on the risks from long-term deliberate systematic exposures to low levels of these materials by hundreds of millions of people. It is safe to say, however, that the people in this room and their work in the last five years probably far exceeds all of the work that has been done in the past 100 years in trying to obtain a better understanding of those possible toxicological endpoints.

Our interest is in three kinds of substances. We are interested in the disinfectants themselves, be they chlorine, ozone, chloramines, iodine or chlorine dioxide, or any other of the particular oxidants. We are also interested in the degradation products of those substances which are retained in the water such as the chlorites, chlorates, hypochlorites, or iodates and whatever additional products there happen to be. We are also interested in the chemical reaction products of those very potent, chemically active substances with the other materials which are in the water. Work has tended to concentrate on the volatile and hydrophobic organic chemicals because of the analytical breakthroughs that have occurred in the last five to seven years, so now there is much more information on the low molecular weight chlorinated by-products than on any others. However, there is very little information on the oxygenated by-products and higher molecular weight or more hydrophylic chemicals, and these make up the greatest portion, by far. The

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presence of these oxidants in the water also alters the oxidation states of many of the other substances that are in the water, be they nitrate instead of nitrite, or higher oxidation states of metals, and many examples where the presence of an oxidant causes a particular chemical specie to be in the water other than would have been there. I suspect that there are many benefits to the disinfection process that we are not aware of apart from disinfection; not the least, for example the question of conversion of nitrites to nitrates in water. The nitrates are probably less toxic than the nitrites, and it just might be that the reason methemoglobinemia is not often detected in high nitrate communities that consume public water is the fact that the water is disinfected. It may be that the presence of oxidizing conditions, including control of reducing organisms, may be a factor in determining susceptibilities, particularly of infants and the risks from water as on exposure route.

One other item that should be examined much more extensively is the *in vivo* chemistry of these substances, particularly the oxidants themselves, and their degradation products after they have been ingested. Beyond investigations of the water chemistry and toxicology of these substances and their byproducts in water, what are the consequences when for example, free chlorine or hypochlorite or chlorite is ingested and combines with proteins, enzymes, hemoglobin, or other macromolecules? There are some important experiments to be performed, and interesting studies of mechanism and effects to be explored. I think that these are some of the things that are going to be examined as this work continues to progress.

Regulatory Activity

From the regulatory standpoint, which is what this discussion was supposed to present, our activities really began in 1974 when the Safe Drinking Water Act passed. One of the reasons the Safe Drinking Water Act passed was because of the great interest and concern about the identification of chlorinated by-products as a result of the use of chlorine in drinking water. The Safe Drinking Water Act provided a number of authorities that never existed before in the United States to control the quality of drinking water. Up until that time, the primary responsibility and the primary control over drinking water quality rested in the hands of the states, and, in fact, to a great degree in the hands of the local communities and the local water treatment plant operators. The idea of the law was to provide a more uniform level of drinking water quality protection throughout the United States

regardless of location and regardless of size of community or financial circumstances.

The law gave EPA two authorities. One of them is to establish acceptable limits for contaminants in drinking water; these are maximum contaminants levels (MCLs). The other had to do with the possibility of requiring specific treatments to be used in drinking water in those cases where maximum contaminant levels were not appropriate. At that time and even now, there are no specific MCLs or treatment requirements that deal with disinfectants, *per se*. There is no disinfection requirement in the United States. The only requirement relative to drinking water and sanitation is the necessity of meeting biological quality standards, the coliform standards. As a matter of option, as a matter of consensus and often of necessity, or state rules, most drinking waters in the United States are chlorinated. There is no national rule that relates to chlorine. Not only is there not an MCL for residual chlorine, there is also not a treatment requirement that demands the use of chlorine. However, two years ago EPA issued a maximum contaminant level for trihalomethanes. The trihalomethanes were the most ubiquitous, most readily identifiable by-products of the chlorination process. The overall guiding principle of the law is that EPA should identify substances in water that may have an adverse effect on health and in general establish MCLs controlling those substances to the extent feasible, taking costs and other factors into consideration (Tables 1 and 2).

Trihalomethanes

I think there has been an inordinant fixation on the fact that the MCL has been established for trihalomethanes. In fact the premise for the regulation and the impetus for its development was to deal with the entire area of disinfection and the use of chlorine. It is only because trihalomethanes happen to be the most readily identifiable markers for the by-products of the chlorination process that the MCL for THM happened to be established. It could have been and it could be in the future modified to reflect other by-products that are produced or some other kind of measurement such as "organically bound halogen." THMs could well be an indicator of the total condition of the water as it is affected by the presence of chlorine.

Figure 1 is a very good illustration of this point. The tip of that iceberg is a very tiny portion of the total amount of by-products that are known to exist. Very few of them have been identified at this point. Trihalomethanes were the most obvious ones among the total organic halogen group. The trihalo-

Table 1. National interim primary drinking water regulations.

Entity	Level
Arsenic	0.05 mg/l.
Barium	1.0 mg/l.
Cadmium	0.010 mg/l.
Chromium	0.05 mg/l.
Lead	0.05 mg/l.
Mercury	0.002 mg/l.
Nitrate (as N)	10 mg/l.
Selenium	0.01 mg/l.
Silver	0.05 mg/l.
Fluoride	1.4 – 2.4 mg/l. (ambient temp)
Endrin	0.0002 mg/l.
Lindane	0.004 mg/l.
Methoxychlor	0.1 mg/l.
Toxaphene	0.005 mg/l.
2,4-D	0.1 mg/l.
2,4,5-TP Silvex	0.01 mg/l.
Coliform bacteria	< 1/100 ml.
Radium-226 + radium-228	5 pCi/l.
Gross alpha particle activity	15 pCi/l.
Beta particle and photon radioactivity	4 mrem (annual dose equivalent)
Turbidity	1 Tu (up to 5 Tu)
Trihalomethanes (the sum of the concentrations of bromodichloromethane, dibromochloromethane, tribromomethane (bromoform) and trichloromethane (chloroform))	0.10 mg/l.
Sodium monitoring and reporting	
Corrosion monitoring and distribution system composition	

Table 2. National secondary drinking water regulations.

Entity	Level
Chloride	250 mg/l.
Color	15 color units
Copper	1 mg/l.
Corrosivity	Noncorrosive
Foaming agents	0.5 mg/l.
Iron	0.3 mg/l.
Manganese	0.05 mg/l.
Odor	3 threshold odor number
pH	6.5 – 8.5
Sulfate	250 mg/l.
TDS	500 mg/l.
Zinc	5 mg/l.

methanes range from as little as 10% or so in some cases up to about 90% of the total organic halogens depending on the specific circumstances. So, obviously there is a great amount unknown on even just the chlorinated by-products or the brominated by-products. In addition, on a mass balance basis the organochlorine products produced during chlorination of water may only account for a few percent of the added chlorine itself and, in fact, the majority of the chemistry of chlorine in water probably is oxidation chemistry rather than chlorination chemistry. So there is a whole host of

Synthetic Organic Chemicals

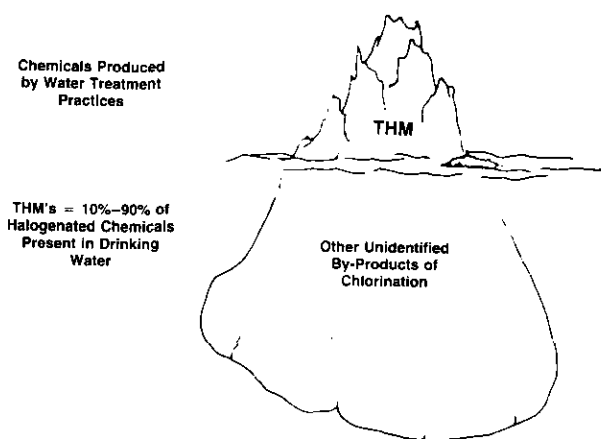


FIGURE 1. Synthetic organic chemicals

by-products for which there is very little information on their identity or toxicology, and which may contribute some increment of human risk. What must be determined, of course, is how significant is that risk and whether there are ways of minimizing it.

The THM regulation is very simple: 0.10 mg/l. for

Table 3. Summary of THM regulations.

Maximum contaminant level (MCL)	0.10 mg/l (100 µg/l.) total trihalomethanes
Applicability	Community water systems that add disinfectant to the treatment process (ground and surface)
Effective:	
Systems > 75,000	2 years after promulgation
Systems 10-75,000	4 years after promulgation
Systems < 75,000	State discretion
Monitoring requirements:	Running annual average of a minimum of 4 samples per quarter per plant taken on same day
	Systems using multiple wells drawing raw water from a single aquifer may, with state approval, be considered one treatment plant for determining the required number of samples.
Effective:	
Systems > 75,000	1 year after promulgation
Systems 10-75,000	3 years after promulgation
Systems < 75,000	State discretion
Sample locations:	25% at extreme of distribution system; 75% at locations representatives of distribution.

the total THMs, and the implementation of that regulation is now in progress. The monitoring requirements in large communities (> 75,000) began (Table 3) in November 1980. The compliance requirements begin November 1981 and following that the sequence continues into smaller communities, down to 10,000 population. Smaller communities are dealt with by state determination.

But why regulate trihalomethanes? After reviewing all of the information, EPA felt there was no question that because of the widespread and extensive use of chlorine, there were a number of reasons why the by-products of chlorination should be controlled, at least by a reasonable first step in that process to reduce obviously unnecessary exposure. It is clear that water chlorination is the major route of exposure to the American population to chloroform and the other trihalomethanes. It is also clear that the most frequently found chemicals in water in almost every community are those trihalomethanes and the other by-products. The concentrations that are found in those waters are among the highest of any synthetic type chemicals that are detected. The risks that are associated with them are not established; they are, however, certainly suggested by the animal toxicology and to a degree by some of the human epidemiology that has been done. It is clear that we actually have a choice—that these chemicals are introduced deliberately and therefore, since they are introduced deliberately, means of control are within reach. The control technology is very common technology, so there is no reason why water systems should not be able to have some effect on the amounts of these materials in finished water. As I said before, the presence of THMs indicates a large number of other chemicals which

Table 4. Uptake of chloroform for the adult human from air, water and food.

Source	Adult uptake, mg/year	Percent uptake
Maximum conditions		
Atmosphere	204	36
Water	343	61
Food supply	16	3
Total	563	100
Minimum conditions		
Atmosphere	0.41	13
Water	0.73	23
Food supply	2.00	64
Total	3.14	100
Maximum-water minimum-air		
Atmosphere	0.41	1
Water	343.00	97
Food supply	9.00	2
Total	352.41	100

are also there and even less understood relative to human risk.

Table 4 gives some numbers on the statement that water is normally the major contributor of these kinds of substances to our total exposure. Under some circumstances (minimum conditions) food intake might contribute more than the water. Under maximum conditions, water contributes more than the food although there can be a substantial portion from inhalation, too. But under conditions of moderate to heavy water exposure and typical atmosphere and typical food supply, the water is, by far, the major contributor. There are very few circumstances in environmental exposure to chemi-

cals where one can pinpoint a route of exposure that so far outweighs the other sources as in this case.

Control of Trihalomethanes

There are many approaches that may be considered in the regulatory context on how to control the trihalomethanes:

- Use of a disinfectant (oxidant) that does not generate (or produces less) THMs in water.
- Treatment to reduce precursor concentrations prior to chlorination.
- Treatment to remove THMs after formation.

Many possible choices exist within each category. For example, alternate disinfectants or oxidants that might be considered include ozone, chlorine dioxide, and chloramines (combined chlorine). Precursor reduction processes include off-line raw water storage, aeration, improved coagulation, ion exchange resins, granular activated carbon (GAC), powdered activated carbon (PAC), and ozone enhanced biological activated carbon (BAC). THM reduction has also been achieved by merely moving the chlorine addition point to later stages in the conventional treatment process, and by substituting prechlorination with some other preoxidation process. THM removal processes include GAC, aeration or macroporous resins.

Modifying disinfection practices is an area of particular interest. A number of other materials can perform as well as chlorine in the treatment of water as disinfectants or oxidants as a part of the total treatment process. But, of course, there are many questions about the toxicology and potential risks from those substances, too. Chlorine and the by-products of chlorination have been studied to a greater degree than ozone, chlorine dioxide and chloramines. These are also used in the United States, but also to a greater degree in other countries (ozone and ClO_2) and there is a long history for all these substances but little information on their toxicology.

The most important principle to remember is that in the course of these fine tuning activities, modifying disinfection practices, modifying dosages, or rearranging treatment processes, we cannot lose sight of the fact that the most significant health risk in drinking water is waterborne disease transmission. There is not only no excuse but there is no reason for taking any kind of action that would reduce the trihalomethanes, but, at some point along the way also increase the risks of waterborne disease. This is one of our great concerns, and, in writing the trihalomethane regulation, we were very cautious to take into consideration what we

felt were the factors that would relate to the application of this regulation in all public water systems around the United States, particularly the small ones where there might be less of an opportunity or capacity for the water system to properly maintain biological quality as well as control chemical quality. So, in the risk-benefit equation, the risk-benefit balance, there should be no factor on the other side of the equation that allows for reduction of trihalomethanes and an increased probability of pathogenic bacteria or viruses being in the water.

Other Oxidants

The next questions to be asked are: what kinds of controls should exist on the use of not only chlorine or chlorine dioxide or other oxidants, or on the amounts of their residuals? At this point there is a recommended limit of 0.5 ppm on the sum of the oxychlorine by-products of chlorine dioxide (except for hypochlorite), and EPA said that, based upon new information, we would reconsider and determine whether an MCL would be appropriate. In the case of ozone, there are no particular restrictions, but we do point out that it is undoubtedly inadvisable to use ozone in many public water systems unless reasonably high quality water has first been produced. There is a very important place for ozone in water treatment, not as a substitute for chlorine, but rather as an integral part of a properly designed complete treatment process.

In the case of chloramines, are there excessive risks introduced by the wider use of chloramines rather than free chlorine? Is the toxicology of chloramines significant in the sense that these are more stable materials that are less likely to decompose early during ingestion and perhaps are going to interact with other systems in the body to a greater degree than some of the more active oxidants would? For example, does residual chlorine decompose in saliva, whereas chloramine might persist to or beyond the GI tract?

Conclusion

We must ask ourselves whether there are long-term risks to the population from consistent widespread exposure to any oxidants in water and their by-products. Are there particular safe levels when considering acute and subchronic and chronic toxicity apart from the carcinogenicity? Are there levels for chlorite, chlorate, chlorine dioxide, chloramines, or whatever in drinking water that should not be exceeded? Are there sensitive elements in the

population that we must be particularly concerned about; those that would be more susceptible than the average person to these kinds of oxidant stresses? Toxicologists and epidemiologists must identify those people and find out what they can tolerate and help us answer these and the following questions. Does the systematic use of chlorine residuals in the United States introduce some additional increment of risk that would not have been there if residuals were not used? But, on the other hand, does the use of residuals add considerable benefits that far outweigh those potential risks? I mentioned the matter of the aerobic nature of the water from the existence of oxidants—are

there particular benefits or particular risks by having an oxidized system rather than a reduced system? On the chemistry and toxicology, are there great similarities between these disinfectants? (Ozone might not produce organochlorine compounds but chlorine produces a vast array of oxidation products just like ozone does.) Are there significantly different products?

So, these are some of the questions that are being examined. One of the top priorities in drinking water health effects research is the matter of oxidants and disinfectants, and the Office of Drinking Water hopes that work will continue very actively.